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MICROSTRUCTURE AND PROPERTIES OF LOWER-TEMPERATURE PORCELAIN

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The technological properties of a series of granite rocks are studied, and it is shown that they can be effectively used as fluxes for porcelain mixes. It is found that low-temperature porcelain can be obtained under intensified heat-treatment. The phase composition, microstructure, and properties of the materials are studied. The effect of the properties of the liquid phase on the formation of structure and the usage and decorative properties of porcelain fabricated by energy-conserving technology are determined.

Key words: lower-temperature porcelain, flux, granites, mullite formation, liquid phase, energy-conserving technology.

Today, the once flourishing porcelain industry in Ukraine is going through difficult times. The production of porcelain dishware is down sharply, and the number of manufacturers has decreased. This situation is largely due to the high cost of gas as the main energy carrier used by ceramic enterprises, the dependence on imports of quartz feldspar raw materials, and inadequate modernization of the industry's technological stock [1].

One promising solution to this problem is to decrease the heat-treatment temperature of porcelain articles while maintaining high aesthetic-use properties and quality. Wide adoption of the low-temperature porcelain technology will give more than a few advantages to domestic manufacturers. The main advantages are lower energy usage and shortening of the technological cycle. This makes the development of new mix compositions for fabricating porcelain articles for household use by means of accelerated low-temperature firing very topical.

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It is known that fluxes — natural materials classified type 1 and 2 fluxes which promote the formation of melt during firing — are usually added to mixes to intensify the sintering of ceramics. Feldspars, pegmatites, leucocratic granites, petalitic rock, nepheline-syenites, and perlites are widely used as fluxes. The use of industrial wastes obtained from the production of low-iron granite rock as a fluxing component in ceramic mixes is economically justified for the production of porcelain articles for household use.

The objective of the present work is to obtain low-temperature porcelain with water absorption $\leq 0.5\%$ and to study the relationship between its properties and structure. Granite siftings obtained during the development of the Anadol'skoe, Kremenevskoe, and Andreevskoe granite deposits (Donetsk Oblast') were used as fluxes in the porcelain mixes with lower-temperature firing; the chemical composition of these granites is presented in Table 1.

The fluxing capacity of the granite rocks chosen for the present investigations was determined using an express method, based on the physical – chemical analysis of rock-forming systems, to determine the composition and proper-

TABLE 1.

Granite deposit	Content, wt.%								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	others
Andreevskoe	70.70	15.70	1.69	0.14	1.60	1.01	4.70	3.86	0.60
Anadol'skoe	71.97	15.97	0.87	0.07	0.81	0.12	3.73	4.48	1.89
Kremenevskoe	70.44	17.35	0.67	0.05	1.62	0.31	4.54	3.70	1.41

TABLE 2.

Melt characteristic	Temperature, °C	Granite deposit		
		Andreevskoe	Anadol'skoe	Kremenevskoe
Amount, %	1150	94.56	93.68	98.20
	1200	97.44	95.11	98.65
	1250	100.00	95.88	99.10
Viscosity (log η), Pa · sec	1150	3.84	3.78	3.67
	1200	3.48	3.46	3.58
	1250	3.40	3.34	3.26
Surface tension, N/m	1150	0.283	0.281	0.287
	1200	0.286	0.289	0.284
	1250	0.289	0.286	0.291
Activity, arb. units	1150	0.091	0.106	0.121
	1200	0.097	0.105	0.122
	1250	0.079	0.104	0.120

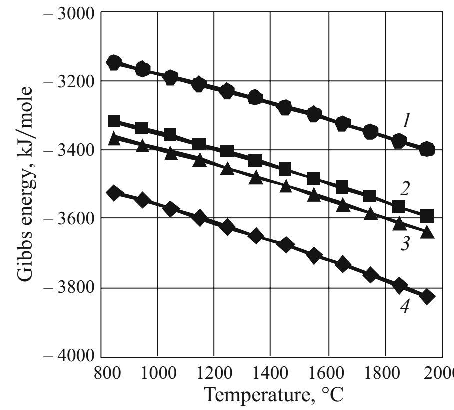

Fig. 1. Temperature dependence of the Gibbs energy of the mullite formation reactions in the porcelain mixes developed (wt.%): *1*) 50 Anadol'skoe granite sifting; *2*) 50 Kremenevskoe granite sifting; *3*) 55 Anadol'skoe granite sifting; *4*) 55 Kremenevskoe granite sifting.

ties of melts formed during heat-treatment of the materials [2]. The viscosity and the surface tension of the rock melts for the temperature interval 1150 – 1250°C were calculated taking account of the additive character of these properties by means of I. A. Makhovskaya's method [3]. The activity of the melts was evaluated by the method proposed by G. Zal'mang [4]. Analysis of the computed properties of the rock melts formed by melting of the granites studied (Table 2) suggests that the rocks with the most effective fluxing action come from the Andreevskoe and Anadol'skoe deposits. These rocks are capable of forming in the temperature interval 1150 – 1250°C melt in amounts 95 – 97% with relatively low viscosity ($10^{3.46} – 10^{3.48}$ Pa · sec) and surface tension within the norms (0.25 – 0.30 N/m) [5].

Kremenevskoe granite forms at 1200°C a larger amount of melt (98.65%) with higher viscosity (log η = 3.58), but compared with Andreevskoe granite it contains less iron oxide, which is a big advantage for obtaining articles with higher whiteness.

A visual examination of the products of firing of the rocks at 1200°C showed that Andreevskoe granite melt has a greenish-grey color, which indicates the presence of darkly colored minerals in the rock. For this reason, granite siftings produced during the development of the Anadol'skoe and Kremenevskoe deposits, were used as the fluxing components in the subsequent development of the porcelain mixes.

The lower-temperature porcelain mixes developed contain the materials: clayey components (white-burning refractory clay from the Dryzhkovskoe deposit and dry-enrichment kaolin from the Glokhovetskoe deposit) and fluxing components (Kremenevskoe and Anadol'skoe granite siftings). The amount of clayey components varied in the range 38 – 43% and the amount of sinter intensifiers was 50 – 55%. A melt modifier (dolomite) in the amount 3% and 5% alumina as an additional source of Al_2O_3, required to form mullite with the participation of excess quartz obtained from the decomposition of kaolinite, were also added to the mixes.

To determine the probability of mullite formation during the formation of lower-temperature porcelain a thermodynamic analysis was performed of this reaction from Al_2O_3 and SiO_2, whose amount corresponds to the molar content in the composition of the porcelain mixes (N_i and M_i):

$$N_i\, Al_2O_3 + M_i\, SiO_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2.$$

The computational results are presented in Fig. 1.

Analysis of the data showed that mullite is likely to form during the heat-treatment of all experimental mixes. The calculation of the phase composition of the products of firing of the mixes developed (Table 3) established that the maximum

TABLE 3.

Flux content in the experimental mix, wt.%		Mullite content, wt.%	Glass phase content, wt.%				Free quartz content, wt.%
Kremenevskoe granite sifting	Anadol'skoe granite sifting		Na_2O	K_2O	Al_2O_3	SiO_2	
50	0	20.03	2.61	2.55	7.06	24.91	31.43
55	0	20.72	2.40	2.44	6.60	23.29	30.62
0	50	13.30	2.20	3.03	6.91	24.39	34.26
0	55	14.59	2.07	2.86	6.45	22.99	34.73

amount of mullite (20.72 wt.%) supposedly forms during the firing of mixes containing 55% Kremenevskoe granite siftings.

Laboratory samples were prepared using a technology that incorporated the slip method of preparing mix, plastic deformation of the mix with 21% moisture content, drying to residual moisture content no more than 2%, and firing in a laboratory muffle furnace with maximum temperatures 1150, 1200, and 1250°C. The degree of sintering of the unglazed fired samples was determined on the basis of the water absorption and the bending strength, the degree of vitrification of the materials was determined from the thickness of the transilluminated layer of material, and the whiteness of the samples was measured on an FB-2 whiteness meter.

Analysis of the properties of the samples of lower-temperature porcelain established the optimal mix compositions, characterized by the same content of Kremenevskoe and Anadol'skoe granite siftings, as well as the conditions under which a prescribed degree of sintering and properties are attained. The materials obtained by firing mixes at 1200°C are characterized by optimal properties: water absorption 0.2 – 0.4%, bending strength 48 – 55 MPa, whiteness 60 – 62%, transilluminated layer thickness 2.85 – 3.05 mm. The temperature 1150°C is too low to obtain porcelain-like materials: samples fired at this temperature have, together with higher whiteness (65%), elevated water absorption ($\geq$ 2%) and are characterized by low translucency of the ceramic (to 1.5 mm). Firing of the materials at 1250°C produces an appreciably lower whiteness (58 – 60%) and bending strength (40 – 45 MPa), higher translucency to 3.5 mm while retaining the prescribed degree of sintering (water absorption $\leq$ 0.5%). At the same time, for compositions containing the maximum amount of flux a negligible increase of water absorption due to the formation of micropores in the glass phase is observed.

The phase composition and structure of the samples with the optimal compositions were studied using x-ray phase and electron-microscope methods of analysis. The XPA results show that the obtained materials are characterized by a high amount of x-ray amorphous matter (glass phase) as well as a substantial amount of crystalline phase, identified as consisting predominately of mullite. Crystals of residual quartz and α-Al_2O_3 not entering into the mullite formation reaction are also present but in negligible amounts.

Fractographic studies of the fired samples of lower-temperature porcelain showed that a sample based on Anadol'skoe granite siftings possesses mainly a large-block structure. Precipitates of the impurity phases in the form of thin interlayers 0.4 – 0.8 μm wide are observed along the boundaries of the blocks. For larger amounts it is evident that the interblock boundary is filled with a mixture of crystalline finely dispersed and semi-amorphous embryos. In contrast to the previous sample, the porcelain based on the Kremenevskoe granite siftings possesses a microblock structure. The interblock boundaries are denser and the impurity precipitates along the boundaries of the blocks are minimal. The electron-microscopic studies showed that the samples are characterized by a fine-grainy structure, consisting primarily of finely dispersed mullite embryos, penetrating the glass phase, as well as isometric grains of quartz, cristobalite, and relic particles of the initial components. It should be noted that the glass phase itself has a liquation character; this is indicated by drop-like inclusions. The study of the structure of the samples made it possible to perform a comparative analysis and to determine the role of the fluxes in the formation of lower-temperature porcelain, since it is known that the composition of the glass phase of porcelain largely determines the structural character of the material.

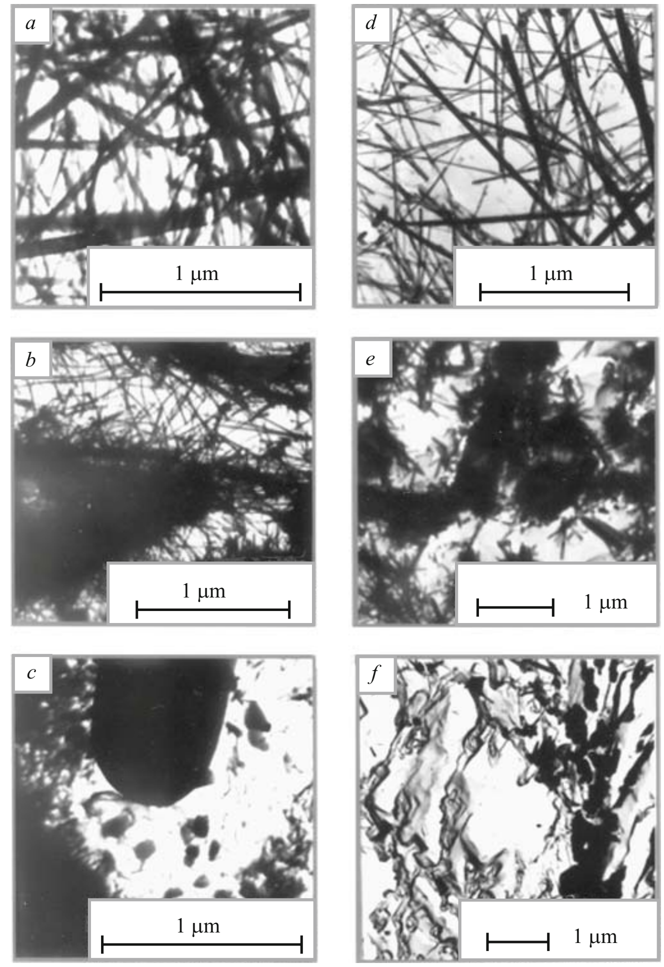

Fig. 2. Electron-microscope photographs of fragments of the structure of lower-temperature quartz: *a*, *b*, *c* and *d*, *e*, *f*) samples based on Anadol'skoe and Kremenevskoe granite siftings.

Additional electron-microscopic studies of the same samples from which the glass phase was pre-extracted by etching were performed to study the effect of the nature of the melt on the formation of the structure of the lower-temperature porcelain. The electron-microscope photographs of the structural elements of the samples obtained on the basis of two different types of siftings are presented in Fig. 2.

Chaotically intertwined mullite crystals, which have a tangled fibrous structure and thereby reinforcing the material, which increases its mechanical strength and decreases its proneness to high-temperature deformation, are seen in the replicas from the sample based on the Anadol'skoe granite siftings (see Fig. 2*a*). The dimensions of the mullite crystals fluctuate from 0.02×4.00 to 0.30×5.00 µm. Mullite forming on residual feldspar grains forms with them a single whole and penetrating into them connects the grains with one another (see Fig. 2*b*). The 0.14 – 0.20 µm grains of the relic quartz are surrounded by a shell consisting of cristobalite grains formed on its outer side (see Fig. 2*c*).

The mullite in ceramic based on the Kremenevskoe granite siftings (see Fig. 2*d*) is finer (the crystal sizes range from 0.20×2.50 to 0.20×3.50 µm), but these crystals are characterized by sharp contours and have a more perfect structure. The needle-shaped mullite crystals penetrate into the glass matrix more uniformly, and there are virtually no felt-like accumulations of crystals. In the present case the smallest needle-shaped mullite crystals make it possible to obtain dispersion-hardened material and they increase the translucency of porcelain. In addition, a much smaller amount of non-regenerated initial materials of small size (see Fig. 2*e*), is observed in the present sample. Figure 2f shows a half-dissolved grain of quartz on whose surface finely dispersed cristobalite can be seen (dark-colored crystals 0.03 – 0.05 µm in size).

The structure of the samples of the lower-temperature porcelain distinguished only by the form of the flux differs appreciably. For example, when Anadol'skoe granite siftings whose melt at 1200°C differs by lower viscosity and activity and higher capability of forming mullite are used in the mixes larger mullite crystal with imperfect structure are observed. When Kremenevskoe granite siftings, which form during heat-treatment under the same conditions a more viscous melt with comparatively low surface tension, are used fine, more perfect mullite crystals form in large quantities in the material, and the elevated activity of the melt gives more complete dissolution of the relic quartz. In addition, such properties of melt create conditions for the formation of submicroscopic needle-shaped mullite crystals which intertwine with one another and penetrate into the glass phase, which on the whole facilities obtaining dispersion-hardened materials.

The structural features established by means of electron microscopy for the materials obtained explain the observed usage and aesthetic indicators. For example, porcelain obtained using Kremenevskoe granite siftings with practically the same water absorption (0.2 and 0.3%, respectively) differs from porcelain based on Anadol'skoe granite siftings by higher whiteness (62%), translucency (0.6% with w.55 mm thick layer), and bending strength (55 MPa).

It can be concluded on the basis of the results obtained in this work that the processes resulting in the formation of the structure and phase composition of lower-temperature porcelain, which proceed with the participation of the glass phase and determine its physical – mechanical properties, are closely related with the properties of the melts formed when the fluxing component of the porcelain mixes melt — viscosity, surface tension, activity, which determines their capacity for dissolving residual quartz and the products of decomposition of clayey components of the mixes. It was also determined that dolomite additions have a positive effect, consisting of acceleration of the process resulting in the formation of the melt and regulating its properties.

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